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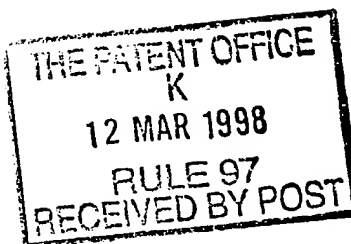
Dated

11 March 1999



# Request for grant of a patent

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The Patent Office

Cardiff Road  
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1. Your reference SMC 60283 12 MAR 1998

2. Patent application number  
(The Patent Office will fill in this part) **9805250.9**

3. Full name, address and postcode of the or of each applicant (underline all surnames) Zeneca Limited  
15 Stanhope Gate  
London  
W1Y 6LN

Patents ADP number (if you know it) 6254007002 ✓

If the applicant is a corporate body, give the country/state of its incorporation United Kingdom

4. Title of the invention WATER SOLUBLE FILMS

5. Name of your agent (if you have one) SHELLER, Alan  
Zeneca Specialties  
Hexagon House  
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Manchester M9 8ZS

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

Patents ADP number (if you know it) 1313642004 ✓

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7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application	Number of earlier application	Date of filing (day / month / year)
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8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

- a) any applicant named in part 3 is not an inventor, or
- b) there is an inventor who is not named as an applicant, or
- c) any named applicant is a corporate body.

See note (d))

# Patents Form 1/77

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Continuation sheets of this form

Description

18

Claim(s)

03

Abstract

Drawing(s)

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents (please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature

*K.M. Pinder*

Date 11/3/98

Zeneca Limited Authorised Signatory

12. Name and daytime telephone number of person to contact in the United Kingdom

K.M. Pinder/C.M. Mottram 0161 721 1361/2

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SMC 60283

APPLICANTS

Zeneca Limited

TITLE

WATER SOLUBLE FILMS

WATER SOLUBLE FILMS

The present invention relates to (preferably cold) water-soluble films suitable for the preparation of water-soluble packaging, e.g. sachets, capsules and bags, and to water-soluble packaging made from such films.

Water-dissolvable packaging, particularly of the type provided by sachets, capsules and bags, have utility for packaging and delivering a range of materials, usually formulated compositions, and particularly formulated compositions which are hazardous (or at any rate unpleasant) to individuals with whom they come into contact or are hazardous or harmful to the environment. Examples include agrochemicals compositions (e.g. insecticides, herbicides, pesticides and fungicides), laundry care products (e.g. detergents, fabric softeners and bleaches), dyestuffs, biocides, industrial or home cleaners, and public health products. The use of water-soluble packaging for packaging certain formulated compositions also provides a convenient way of adding a measured dosage of the formulation for subsequent dilution with water in order to provide the desired final concentration of the diluted formulation.

Polyvinyl alcohol (PVA) has been widely utilised for the preparation of water dissolvable film for the production of sachets for packaging hazardous materials such as agrochemicals; methyl cellulose is also widely utilised (see e.g. WO 93/22215). Such polymers however have limitations. For example, the films tend to be blocky when damp. In addition it is necessary to incorporate plasticisers to achieve the desired level of flexibility; plasticisers can migrate out of the film to render it brittle and can further increase the risk of blocking. Still further, the presence of reactable hydroxyl groups in such films restricts their use for packaging hydroxyl-reactive compounds. Yet still further such films are insolubilised by borates (used in laundry care).

It has also been proposed to employ carboxylated acrylic polymers for making water-dissolvable films for the production of water-soluble packaging (sachets, and the like). Such films, however, may not always have satisfactory wet handling properties or may not always retain their mechanical properties in humid environments.

We have now discovered certain polyurethane films which are water-soluble and eminently suitable for the provision of water-dissolvable packaging (sachets, capsules, bags etc) for packaging. Such films, can e.g, have improved solubility in cold water compared to conventional PVA films; also unlike the PVA films, there is no need for externally added plasticiser (although plasticiser can be added if desired). Such films also have superior wet handling characteristic properties and better mechanical properties in humid environments than carboxylated acrylic films.

According to the present invention there is provided a water-soluble film comprising a polyurethane polymer(s) having polyethylene oxide groups and acid-functional group wherein :

the polyoxyethylene oxide groups are present in the polyurethane polymer in an amount which is within the range of 5 to 45 wt % based on the weight of polyurethane polymer and have a chain length(s) corresponding to a number average molecular weight within the range of 200 to 5000 Daltons;

5 the acid-functional groups are present in the polyurethane in an amount which provides 15 to 150 milliequivalents of such groups per 100 g of polyurethane polymer;  
at least a proportion of the acid-functional groups are neutralised, such neutralisation being with a base(s) at least part of which is a non-volatile base(s);  
and said polyurethane polymer is the reaction product of

10 (A) an isocyanate-reactive prepolymer component comprising an isocyanate-terminated polyurethane prepolymer, said component being formed from reactants which comprise :

- (i) at least one organic polyisocyanate;
- (ii) at least one isocyanate-reactive compound providing said  
15 polyethylene oxide groups in the resulting polyurethane polymer;  
and
- (iii) at least one isocyanate-reactive compound providing said  
acid-functional groups in the resulting polyurethane polymer,

and

20 (B) an active hydrogen component comprising an active hydrogen chain-extending compound(s)

The polyurethane films of the invention are normally made from an aqueous solution of the polyurethane, e.g. by casting. Alternatively dry polymer may be recovered from an aqueous solution (e.g. by spray drying or freeze drying, whereby any cosolvent  
25 used in its synthesis can be removed) and the film then formed by a) redissolving the polymer in water and applying (casting, spraying or doctor blading) to a substrate or b) melt processing (e.g. slit extension or blown film formation).

Therefore there is further provided according to the invention an aqueous solution of a polyurethane polymer as defined supra.

30 There is further provided according to the invention water-soluble packaging, particularly a sachet, capsule or bag, in which the enveloping film of the packaging comprises a polyurethane polymer film as defined supra.

There is further provided according to the invention the use of packaging as defined supra for packaging a material.

35 There is further provided according to the invention the combination of a water-soluble packaging as defined supra and a material packaged therein.

It has been proposed in JP-A-2102225 to use certain polyurethane polymers containing polyethylene oxide groups and optionally (inter alia) acid-functional groups for the provision of water-soluble films for packaging. Such polyurethanes, however, are not

formed by a prepolymer chain-extension process, have polyoxyethylene oxide groups with molecular weight of 6000 or more, and may contain acid-functional groups which if present are preferably at a very low level. The resulting films are inferior to those of the present invention, particularly with regard to inferior mechanical properties (resulting from the lack of a chain extension step in the urethane synthesis) and are also very soft, with the softness being very humidity dependent (in view of the solubilising groups being exclusively or mainly polyoxyethylene groups).

Water-soluble films formed from certain polyurethane polymers have also been disclosed in JP-A-6032976, where such polymers are derived from polyoxyethylene polyols and polyisocyanates. The polyoxyethylene group content in such polyurethanes is at least 50 wt %, and there is no disclosure or suggestion that acid groups should also be present. The resulting films are inferior to those of the present invention (e.g. having inferior mechanical properties due to the very high amount of polyethylene oxide groups).

It is preferred that the polyurethane film is cold water-soluble since it may be difficult in some applications (e.g. large scale outdoor use as might be encountered when dispensing agrochemical materials) to provide hot water for dissolving the packaging. Cold water-soluble means herein soluble in water at temperatures  $\leq 35^{\circ}\text{C}$ , and generally between 5 and  $35^{\circ}\text{C}$ . (Note that if the film is cold water-soluble it will usually be hot water soluble as well, i.e. soluble at water temperatures  $> 35^{\circ}\text{C}$  - e.g. up to  $70^{\circ}\text{C}$  or above).

The polyethylene oxide (hereinafter PEO) groups are present in the polyurethane polymer in an amount within the range 5 to 45 wt % based on the weight (dry) of the polyurethane polymer, preferably 5 to 40 wt %, more preferably 7 to 35 wt %.

The PEO chains may be in-chain in the polyurethane polymer, or may be chain-pendant to the urethane backbone, or some may be in-chain and some may be chain-pendant. Also some of the PEO groups may be chain-terminal, e.g. at the end of a urethane chain or capping a pendant group. Usually, the PEO units are in-chain. The PEO groups significantly contribute to the water-solubility of the film.

The molecular weight of the PEO groups should be within the range of 200 to 5000 Daltons, preferably 400 to 3000 Daltons, and more preferably 500 to 2000 Daltons.

PEO groups are normally introduced into the polyurethane by employing in the polyurethane prepolymer synthesis an isocyanate-reactive compound incorporating a polyoxylene chain(s) as a group(s) therein. Preferably, the isocyanate-reactive group is a hydroxyl group, and polyols, diols, and (in some cases) monohydroxy compounds may be used; preferably diols are employed. Typically the isocyanate-reactive compound is a polyoxyethylene polyol, particularly a polyoxyethylene diol. Poxoxyethylene diols may be made e.g. by polymerisation of ethylene oxide under aqueous alkaline conditions, or by the addition of ethylene oxide to an initiator such as water, ethylene glycol or propylene glycol, or by the condensation polymerisation of ethylene glycol (to produce poly(ethylene glycol)). Such synthetic procedures are all well known to the art.



The use of polyoxyethylene diols will form in-chain PEO groups. Chain-pendant PEO groups may be introduced by employing in the prepolymer synthesis diols having pendant PEO chains, e.g. those described in US 3905929. In US 3905929 examples of such compounds are disclosed which may be obtained by reacting one mole of an organic diisocyanate in which the two isocyanate groups have different reactivities with approximately one mole of a polyethylene glycol mono-ether and then reacting the adduct so obtained with approximately one mole of a dialkanolamine, for example diethanolamine. Chain-pendant PEO groups may also be introduced by employing in the prepolymer synthesis certain amine and hydroxyl functional compounds, or diols, as disclosed in EP 0317258, where such compounds are obtained by oxyalkylating a defined polyether amine containing PEO residues.

The polyurethane polymer may optionally, but in many cases usefully, incorporate polypropylene oxide (hereinafter PPO) chains, which, as for the PEO chains, may be in-chain, chain-pendant or both in-chain and chain-pendant (and sometimes may also be terminal); usually the PPO chains (as with the PEO chains) are in-chain. The presence of PPO chains can advantageously improve the hardness of the film without excessively sacrificing good water solubility.

PPO groups may be introduced in the same manner as described above for introducing PEO groups, but using the analogous PPO-resulting compounds instead of PEO-resulting compounds in the prepolymer synthesis (e.g. to produce polypropyleneoxide diols, one may polymerise propylene oxide, or add propylene oxide to an initiator, or one may condensation polymerise propylene glycol to form poly(propylene glycol)). Chains containing both PEO and PPO units may also be used for incorporating the PEO and PPO groups, e.g. poly(oxyethylene-oxypropylene) diols obtained by the simultaneous or sequential addition of ethylene and propylene oxides to appropriate initiators.

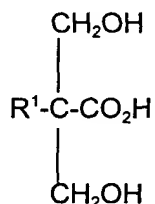
PPO groups are preferably present in the polyurethane polymer in amount 0 to 45 wt %, based on the (dry) weight of the polyurethane polymer, more preferably 5 to 40 wt %, more preferably 10 to 35 wt %. The number average molecular weight of the PPO chains, if present, should preferably be within the range of 200 to 5000 Daltons, more preferably 400 to 5000 Daltons, more preferably 500 to 3000 Daltons.

The organic polyisocyanate used in making the prepolymer may be an aliphatic, cycloaliphatic, araliphatic or aromatic polyisocyanate. Normally diisocyanates are employed. Examples of suitable diisocyanates include ethylene diisocyanate, 1,6-hexamethylene diisocyanate, isophorone diisocyanate, cyclohexane-1,4-diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, cyclopentylene diisocyanate, p-tetra-methylxylene diisocyanate (p-TMXDI) and its meta isomer (m-TMXDI), 2,6-toluene diisocyanate (and its hydrogenated derivative), 4,4'-diphenyl-methane diisocyanate (and its hydrogenated derivative), 2,4'-diphenylmethane diisocyanate (and its hydrogenated derivative),

polymethylene polyphenyl polyisocyanates and 1,5-naphthylene diisocyanate. Mixtures of polyisocyanates can be used, particularly isomeric mixtures of the toluene diisocyanates or isomeric mixtures of the diphenylmethane diisocyanates (or their hydrogenated derivatives), and also polyisocyanates which have been modified by the introduction of urethane, allophanate, urea, biuret, carbodiimide, uretonimine or isocyanurate residues. Preferred polyisocyanates are cycloaliphatic polyisocyanates such as isophorone diisocyanate, p-TMXDI, m-TMXDI and 4,4'-dicyclohexylmethane diisocyanate, and aliphatic diisocyanates such as 1,6-hexamethylene diisocyanate.

The isocyanate-reactive compound for providing acid-functional groups used in the prepolymer synthesis is preferably an acid-bearing polyol, particularly a diol, and preferably of low molecular weight (<500). The acid groups may e.g. be selected from carboxylic acid, sulphonic acid, sulphuric acid and phosphoric acid groups; when neutralised these yield corresponding anionic groups, viz  $-\text{CO}_2^-$ ,  $-\text{SO}_3^-$ ,  $-\text{OSO}_3^-$  and  $-\text{PO}_2^-$ . Preferably, the acid group is a carboxylic acid or sulphonic acid group, but more particularly is a carboxylic acid group (providing a carboxylate anion  $-\text{CO}_2^-$  on neutralisation).

Particularly preferred carboxylic acid-bearing polyols are dihydroxyalkanoic acids of formula



where  $\text{R}^1$  is hydrogen or alkyl (usually 1-5C). The most preferred carboxyl-bearing polyol is 2,2-dimethylol propionic acid (DMPA).

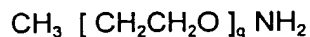
The isocyanate-reactive compound(s) for providing acid-functional groups is preferably used in an amount which provides 15 to 150 milliequivalents of such groups per 100g of polyurethane polymer, preferably 30 to 125 milliequivalents more preferably 45 to 115 milliequivalents per 100 g of polymer.

In the case where DMPA is used for providing the acid functional groups, the polyurethane polymer usually contains 2 to 20 wt % of units derived from this compound, more preferably 5 to 15 wt %.

Besides contributing to water-solubility, the presence of acid groups in the polyurethane also provides improved hardness of the film.

The reactants used to form the prepolymer component may optionally include a compound(s) which is monofunctional with regard to isocyanate-reactive functionality. Such a compound will act as a chain-capping material, i.e. will act as a chain terminator. Accordingly, if used, some of the prepolymer component will include polymer chains

which are only terminated at one end by an isocyanate group, with the other end being inert to isocyanate-reactive groups. Therefore such chains in the prepolymer compound will not, unlike the fully isocyanate-terminated prepolymer, (i.e. terminated at each end by isocyanate groups), undergo chain extension, and this may usefully be employed to control the molecular weight of the final chain-extended polymer. Examples of such compounds include polyethylene oxide compounds capped at one end by an inert group (e.g. alkoxy, such as methoxy) and at the other by an isocyanate-reactive group such as amino (preferably primary amino), for example,



where q can go from, for example, 4 to 120.

The polyurethane polymer may also optionally (but less preferably) include units from other isocyanate-reactive compounds that are introduced during the prepolymer synthesis. These are usually diols, although diamines may e.g. alternatively or additionally be used. Examples of these compounds include polymeric diols having molecular weights in the range 400-6000. Such diols may be members of any of the chemical classes of polymeric diols used or proposed to be used in polyurethane formulations. In particular, the diols may be polyesters, polyesteramides, polyethers (other than ones providing PEO and/or PPO groups), polythioethers, polycarbonates, polyacetals, polyolefins or polysiloxanes. Preferred polyol molecular weights are from 700 to 2000.

Other examples of optional diols used in the prepolymer synthesis include organic diols having molecular weights below 400. Examples of such lower molecular weight diols include ethylene glycol, diethylene glycol, tetraethylene glycol, bis(hydroxyethyl) terephthalate, cyclohexane dimethanol, and furan dimethanol.

The polyurethane prepolymer may be prepared in conventional manner by reacting the organic polyisocyanate and isocyanate-reactive (usually entirely or mainly polyol) components under substantially anhydrous conditions at a temperature between about 30°C and about 130°C until reaction between the isocyanate groups and the isocyanate-reactive (usually all or mainly hydroxyl) groups is substantially complete. Since the prepolymer is to be wholly or substantially isocyanate-terminated it follows that a stoichiometric excess of the organic polyisocyanate component over the isocyanate-reactive component should be employed. Preferably the reactants are used in amounts corresponding to a ratio of isocyanate groups to isocyanate-reactive (usually hydroxy) groups of from 1.1:1 to 2:1, more preferably from 1.3:1 to 1.8:1 which has provided particularly good results.

If desired, catalysts such as dibutyltin dilaurate, stannous octoate, or certain tertiary amines may be used to assist prepolymer formation. An organic solvent may

optionally be added before, during or after prepolymer formation to control the viscosity. Suitable solvents which may be used include acetone, methylethylketone, dimethylformamide, diglyme, N-methylpyrrolidone, 1-methyl-2-pyrrolidinone, ethyl acetate, ethylene and propylene glycol diacetates, alkyl ethers of ethylene and propylene glycol diacetates, alkyl ethers of ethylene and propylene glycol monoacetates, toluene, xylene and sterically hindered alcohols such as t-butanol and diacetone alcohol. The preferred solvents are water-miscible solvents such as N-methylpyrrolidone, acetone and dialkyl ethers of glycol acetates or mixtures of N-methylpyrrolidone and methylethylketone.

As mentioned above the polyurethane films are normally made from an aqueous solution of the polyurethane, and it is therefore preferred to synthesis the polyurethane using a process whereby an aqueous solution results from the synthesis; this is then ready for use in preparing a film (possibly with concentration or dilution if desired). (Alternatively, it would be possible to convert the polyurethane solution to a dry polymer and reconstitute an aqueous polyurethane solution at a later time). It is to be understood that such aqueous polyurethane solutions may be cloudy as well as clear, the former case indicating the presence of a small amount of dispersed (i.e. not dissolved - probably swollen) polymer even though by far the major part of the polymer is dissolved. Such cloudy solutions can nevertheless still provide water-soluble films, and the term "solution" is intended to extend to cloudy solutions.

Accordingly there is further provided according to the invention a process for the production of an aqueous polyurethane polymer solution, which polyurethane polymer has polyethylene oxide groups and acid-functional groups and wherein:

the polyoxyethylene oxide groups are present in the polyurethane polymer in an amount which is within the range of 5 to 45 wt % based on the weight of polyurethane polymer and have a chain length(s) corresponding to a number average molecular weight within the range of 200 to 5000 Daltons;

the acid-functional groups are present in the polyurethane in an amount to provide 15 to 150 milliequivalents per 100 g of polyurethane polymer; and

at least a proportion of the acid functional groups are neutralised, such neutralisation being with a base(s) at least part of which is a non-volatile base(s);

said process comprising:

I synthesising an isocyanate-reactive prepolymer component comprising an isocyanate-terminated polyurethane prepolymer, said component being formed from reactants which comprise:

- (i) at least one organic polyisocyanate,
- (ii) at least one isocyanate-reactive compound providing said polyethylene oxide groups in the resulting polyurethane polymer, and
- (iii) at least one isocyanate-reactive compound providing said acid-functional groups in the resulting polyurethane polymer;

- II chain extending the prepolymer component using an active hydrogen component comprising an active hydrogen chain extending compound(s) to form said polyurethane polymer; and
- III forming an aqueous solution of said polyurethane polymer.

5 The stages II and III of the process are not necessarily carried out sequentially or as individual steps. For example, the chain extension step may be carried out simultaneously with the formation of the aqueous polyurethane polymer solution by dispersion of the polyurethane prepolymer into an aqueous medium containing the active hydrogen component, or into an aqueous medium into which the active hydrogen component is subsequently incorporated. Dispersion of the prepolymer into water would  
10 form a solution of the prepolymer if sufficient of the acid groups had already been neutralised at that stage, so that a final polyurethane in aqueous solution would result after chain extension. It would, however, also be possible for a dispersion (rather a solution) of the prepolymer to be formed on dispersion into water if insufficient of the acid groups had been neutralised at that stage; further neutralisation by the addition of more  
15 bases(s) before, during, or after chain extension (or over one or more of these periods) could then be effected so as to provide an aqueous solution of the final polyurethane polymer.

An aqueous polyurethane solution is preferably prepared by forming an aqueous  
20 solution of the polyurethane prepolymer component by dispersing it (optionally carried in an organic solvent medium) in an aqueous medium, preferably utilising only the self-dispersibility properties of the prepolymer arising from the acid anion groups and nonionic groups although free surfactant(s) may additionally be employed if desired (however, as mentioned above, a dispersion rather than a solution may be formed at this stage with  
25 further neutralisation taking place subsequently - before, during or after chain extension, or over one or more of these periods) and chain extending the prepolymer with an active hydrogen component in the aqueous phase, the active hydrogen component being present in the aqueous phase during dispersion or added subsequently (i.e. chain-extension can take place during and/or after the dispersion into water in this embodiment).

30 The prepolymer may be dispersed in water using techniques well known in the art. Preferably, the prepolymer is added to the water with agitation or, alternatively, water may be stirred into the prepolymer.

Alternatively, although less preferably, the prepolymer may be chain extended to  
35 form the polyurethane polymer while dissolved in an organic solvent (usually acetone) followed by the addition of water to the polymer organic solution until water becomes the continuous phase and the subsequent removal of solvent (e.g. by distillation) to form an aqueous solution (or initially a polymer dispersion followed by further neutralisation to

form a polymer solution - as discussed above *mutatis mutandis*) (the well-known "acetone process").

It will be apparent from the above discussion that neutralisation of the acid groups with a base(s) may be effected at any convenient stage of the synthesis and may be done over one or more stages. For example, neutralisation of acid groups may be effected at the prepolymer synthesis stage prior to (i.e. by neutralising the acid monomer), during or subsequent to the formation of the prepolymer (or over one or more of these stages) so that the prepolymer prior to chain extension is water-soluble or can form a dispersion in water (with further neutralisation being necessary in the latter case either of the prepolymer or of the final polyurethane to provide an aqueous polyurethane solution). Where neutralisation is effected subsequent to the synthesis stage of the prepolymer, this can e.g. be done by dispersing the prepolymer into water in parallel with a base(s) or into water containing a base(s) or to which a base(s) is subsequently added (to form a solution or dispersion as discussed above, the latter case requiring further neutralisation subsequently as discussed above). Such neutralisation may be carried out prior to and/or during and/or after the chain-extension step, depending on what stage(s) the active hydrogen component is incorporated with the water, with further neutralisation if necessary taking place after chain-extension in some embodiments (see *supra*).

The active hydrogen chain extender compound(s) of the active hydrogen component which may be reacted with the prepolymer is suitably a primary or secondary aliphatic, alicyclic, aromatic, araliphatic or heterocyclic diamine or polyamine, or hydrazine or a substituted hydrazine. Water-soluble chain extenders are preferred.

Water itself may be used as an indirect chain-extender (although not when using the "acetone process") because it will slowly convert some of the terminal isocyanate groups of the prepolymer to amino groups and the modified prepolymer molecules will then act as a chain-extender for the unreacted isocyanate-terminated prepolymer molecules. However this is very slow compared to chain-extension using the above mentioned active hydrogen chain extenders which will provide the predominant chain-extension reaction if used.

Examples of such chain extenders useful herein include ethylene diamine, diethylene triamine, triethylene tetramine, propylene diamine, butylene diamine, hexamethylene diamine, cyclohexylene diamine, piperazine, 2-methyl piperazine, phenylene diamine, tolylene diamine, xylylene diamine, tris (2-aminoethyl) amine, 3,3'-dinitrobenzidine, 4,4'-diaminodiphenylmethane, methane diamine, m-xylene diamine, isophorone diamine, and adducts of diethylene triamine with acrylate or its hydrolysed products. Also amine terminated polyethylene glycols (i.e. polyethylene glycol diamines) such as the "Jeffamine" ED series; the structure of these materials is given by the manufacturers as  $\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2[\text{OCH}(\text{CH}_3)\text{CH}_2]_a[\text{OCH}_2\text{CH}_2]_b[\text{OCH}_2\text{CH}(\text{CH}_3)\text{NH}_2]_c$  where  $a + c = 2.5$  and  $b$  is available at different values. Also materials such as hydrazine

(e.g. in the form of its mono hydrate), azines such as acetone azine, substituted hydrazines such as, for example, dimethyl hydrazine, 1,6-hexamethylene-bis-hydrazine, carbodihydrazine, hydrazides of dicarboxylic acids and sulphonic acids such as adipic acid dihydrazide, oxalic acid dihydrazide, isophthalic acid dihydrazide, hydrazides made  
5 by reacting lactones with hydrazine such as gamma hydroxylbutyric hydrazide, bis-semi-carbazide, and bis-hydrazide carbonic esters of glycols. Preferably the chain extender in hydrazine (or its monohydrate) or ethylene diamine.

Where the chain extender is other than the modified prepolymer molecules formed by reaction with water (assuming the prepolymer dispersion into water embodiment is  
10 being used) for example a polyamine or hydrazine, it may in preferred embodiments be added to the aqueous solution (or dispersion) of prepolymer or, alternatively, it may already be present in the aqueous medium when the prepolymer is dispersed therein.

The active hydrogen component, besides containing chain-extending material, can optionally include a reactant(s) which is monofunctional with regard to isocyanate-reactivity. Such material(s) in the active hydrogen component will act as a chain-capping  
15 material, i.e. will act as a chain terminator. Such materials may usefully be employed to control molecular weight of the final chain-extended polyurethane.

Examples of such compounds include  $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$  and  $\text{CH}_3\text{O}(\text{CH}_2\text{CH}_2\text{O})_m(\text{CH}_2\text{CH}(\text{CH}_3))_y\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_2$ , where e.g. n can be 1 to 100, m can  
20 be 10 to 100 and y can be 2 to 15.

The chain extension can be conducted at elevated, reduced or ambient temperatures. Convenient temperatures are from about 5°C to 90°C, more preferably 10 to 60°C.

The total amount of active hydrogen component employed (other than water)  
25 should be approximately equivalent to the free-NCO groups in the prepolymer component, the ratio of isocyanate-reactive groups in the active hydrogen chain extender component to NCO groups in the prepolymer component preferably being in the range from 0.5/1 to 1.8/1, more preferably 0.7/1 to 1.5/1. When chain-extending using hydrazine, we have found that good mechanical properties are often obtained at a ratio  
30 such that 70-85 mole % of the terminal isocyanate groups are reacted with hydrazine. Of course, when water is employed as an indirect chain extender, these ratios will not be applicable since the water, functioning both as an indirect chain extender and a dispersing medium, will be present in a gross excess relative to the free-NCO groups.

The resulting polyurethane polymer (after chain extension) will often have a  
35 number average weight within the range of 2000 to 50000 Daltons (however this is a very difficult property to measure in the invention polymers).

[It is evident from the foregoing that the term "polyurethane" as used in this specification is intended to apply not only to polymers (or prepolymers) made by reacting only polyisocyanates and polyols to give urethane linkages, but also the polymers (or

prepolymers) made by reacting polyisocyanates with other types of compound, in conjunction with polyols, having other types of isocyanate-reactive groups, thereby to give polymers, prepolymers or polymer segments comprising other types of linkages, for example urea or amide linkages].

5           With further regard to the neutralisation of the acid-functional groups, the neutralisation of at least a proportion thereof is brought about by the use of a base(s), at least part of which is non-volatile base(s) so as to convert the desired proportion of acid-functional groups to anionic salt groups together with the corresponding presence of cations derived from the base(s). Preferably at least 50%, more preferably at least 90%,  
10   of the acid-functional groups in the final product are neutralised. At least a proportion of the base(s) used for neutralisation should be of the non-volatile type, preferably at least 50 wt % (based on the total weight of base(s) used), more preferably at least 90 wt %, and particularly 100 wt % (i.e. all non-volatile base(s) and no volatile base(s)) since volatile bases might be lost during film formation and storage of the films - leading to poor  
15   water-solubility. Bases which are of the non-volatile (i.e. permanent) type include the Group IA monovalent metal bases or basic salts, e.g. hydroxides, bicarbonates or carbonates (as appropriate) and particularly the hydroxides of Na, K and Li, and non-volatile water-soluble organic bases such as triethanolamine and 2-methyl-2-amino-1-propanol. The most preferred permanent base is NaOH. Examples of volatile bases, if  
20   used, include ammonia and volatile aliphatic amines such as triethylamine and diethanolamine.

          The amount of permanent base used may usefully in some circumstances be in excess of the amount of base(s) required to neutralise all of the acid-functional groups in the polyurethane polymer so that the resulting film contains residual permanent base from  
25   the neutralisation. The presence of such residual base in the film can provide a greater rate of dissolution in water. The amount of non-volatile base from neutralisation remaining in the film in such an embodiment is preferably up to 10 wt %, based on the weight of the film.

          In a further embodiment of the invention the polymeric material providing binder  
30   material of the water-soluble film of the invention includes besides a polyurethane polymer(s) as defined supra a different polymer(s) which is other than a polyurethane but must not detract from the water-solubility of the resulting film.

          Examples of such other polymers include PVA's, polyethylene oxide, starches, gelatin, cellulose such as cellulose ethers (e.g. carboxymethyl cellulose and methyl  
35   cellulose) and hydrophobically modified cellulose, and, more particularly carboxyl-functional vinyl polymers, preferably carboxyl-functional acrylic polymers whose carboxyl groups must be at least partly neutralised in order to provide the necessary water-solubility.



Where a polymer(s) other than a polyurethane is included in the polymeric material of the film, it is preferably present in an amount of up to 70 wt %, based on the combined dry weight of all polymeric material of the film, more preferably up to 50 wt %, and still more preferably up to 40 wt %.

5 Preferably, as mentioned above, the other polymer (if used) is a carboxyl-functional vinyl polymer, and the polyurethane and vinyl monomers may be brought together by any suitable technique.

For example, it would be possible to simply blend together dry polymers and make an aqueous solution thereof for film formation, or effect film formation by melting  
10 processing of the dry blend. In another method, an aqueous solution of the polyurethane and an aqueous solution of the vinyl polymer, separately prepared, may be blended together (with agitation if necessary). In another method, the polyurethane prepolymer could in principle be dispersed into an aqueous solution of a preformed vinyl polymer with simultaneous or subsequent chain extension of the prepolymer.

15 More preferred, however, is to perform the preparation of the vinyl polymer *in-situ* in the presence of the polyurethane polymer during and/or after its formation. In such an embodiment the vinyl monomer(s) for making the vinyl polymer may be introduced in the process of at any suitable stage. For example, where an aqueous solution of the prepolymer is formed in the process to make the polyurethane polymer (as is preferred)  
20 all of the vinyl monomer(s) may be added to the prepolymer prior to its dispersion into water, or all of the vinyl monomer(s) may be added subsequent to the dispersion, or part of the monomer(s) may be added to the prepolymer prior to dispersion and the remainder added subsequent to dispersion. In the case where all or part of the monomer(s) is added to the prepolymer prior to dispersion into water, such monomer(s) could be added  
25 to the prepolymer subsequent to its formation or prior to its formation, or some could be added subsequent to its formation and some added prior to its formation. In the case where any vinyl monomer(s) is added prior to the prepolymer formation it may usefully provide at least part of a solvent system for the reaction to form the prepolymer (if it possesses suitable solvent characteristics). This is particularly advantageous in that it  
30 may replace, in part or in total, difficult - to - remove organic solvents (such as N-methyl pyrrolidone) which are often included to control prepolymer viscosity; since the vinyl monomer(s) is subsequently polymerised, the need for physical removal from the system does not arise.

The vinyl polymer of the invention composition is normally made by an aqueous  
35 free-radical polymerisation process. When made *in-situ*, and where an aqueous solution of the polyurethane prepolymer is formed in the process to make the polyurethane polymer, with chain extension being carried out in the aqueous phase (as is preferred), the vinyl polymerisation may be performed simultaneously with the chain extension step, or performed subsequent to the chain extension step, or performed partly simultaneously

with the chain extension step and partly subsequent to the chain extension step. If the "acetone process" is adopted for making the polyurethane polymer (see above for a discussion of this technique) wherein chain extension occurs in an organic solvent phase (usually acetone), the vinyl polymerisation is normally performed subsequent to the chain extension step after removal of solvent to form an aqueous solution of the polyurethane polymer (although it would, in principle, be possible to perform the vinyl polymerisation in the solvent, disperse the urethane/vinyl polymer into water, and then remove the solvent).

All of the vinyl monomer(s) to be polymerised may be present at the commencement of the vinyl polymerisation, or alternatively in cases where all or part of the monomer(s) to be polymerised has been introduced subsequent to the formation of an aqueous polyurethane prepolymer solution, or, in the case of using the "acetone process", normally subsequent to the formation of the chain extended polyurethane aqueous solution (although it would, in principle, be possible to add the vinyl monomer(s) at the prepolymer formation stage), some or all of that monomer(s) may be added to the reaction medium during the course of the polymerisation (in one or more stages or continuously).

By a vinyl polymer herein is meant a homo or copolymer derived from the addition polymerisation (using a free radical initiated process and usually in an aqueous medium) of one or more olefinically unsaturated monomers. To provide adequate water-solubility characteristics, the vinyl polymer is preferably formed from a monomer mixture which contains 5 to 40 wt % of acid functional monomer(s), more preferably 8 to 15 wt %, and still more preferably 8 to 14 wt % (based on the total weight of vinyl monomers used for the polymerisation).

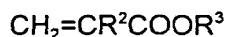
Particularly preferred vinyl polymers are acrylic polymers, i.e. based predominantly on at least one ester of acrylic or methacrylic acid, and with the acid groups preferably being provided by acrylic acid and/or methacrylic acid.

The polymerisation of the at least one vinyl monomer to form the vinyl polymer will require the use of a free-radical-yielding initiator(s) to initiate the vinyl polymerisation. Suitable free-radical-yielding initiators include inorganic peroxides such as K, Na or ammonium persulphate, hydrogen peroxide, or percarbonates; organic peroxides, such as acyl peroxides including e.g. benzoyl peroxide, alkyl hydroperoxides such as t-butyl hydroperoxide and cumene hydroperoxide; dialkyl peroxides such as di-t-butyl peroxide; peroxy esters such as t-butyl perbenzoate and the like; mixtures may also be used. The peroxy compounds are in some cases advantageously used in combination with suitable reducing agents (redox systems) such as Na or K pyrosulphite or bisulphite, and i-ascorbic acid. Azo compounds such as azoisobutyronitrile may also be used. Metal compounds such as Fe.EDTA (EDTA is ethylene diamine tetracetic acid) may also be usefully employed as part of the redox initiator system. We particularly prefer to use an initiator system partitioning between the aqueous and organic phases, e.g. a combination

of t-butyl hydroperoxide, iso-ascorbic acid and Fe.EDTA. The amount of initiator or initiator system to use is conventional, e.g. within the range of 0.05 to 6 wt % based on the total vinyl monomer(s) used.

An aqueous vinyl polymerisation carried out in the absence of the polyurethane normally needs to be performed in the presence of a stabilising and/or dispersing material, and when making an aqueous latex of a vinyl polymer (which after polymerisation can be converted to a solution by neutralisation of carboxyl groups), a conventional emulsifying agent would need to be employed (e.g. anionic and/or non-ionic emulsifiers such as Na salts of dialkylsulphosuccinates, Na salts of sulphated oils, Na salts of alkyl sulphononic acids, Na, K and ammonium alkyl sulphates, C<sub>22-24</sub> fatty alcohols, ethyloxylated fatty acids and/or fatty amides, and Na salts of fatty acids such as Na stearate and Na oleate; the amount used is usually 0.1 to 5% by weight on the weight based on the total olefinically unsaturated monomer(s) used). When incorporated using an in-situ process, however, the polyurethane polymer containing anionic (and optionally nonionic) dispersing groups usually removes the requirement for the use of a separately added conventional emulsifying agent since the polyurethane itself acts as an effective dispersant for the vinyl polymerisation, although a conventional emulsifier can be still employed if desired. (Indeed it may be mentioned that it is often very difficult, and sometimes impossible, to incorporate acid functional monomers in in-situ acrylic polymerisations (because of colloid instability leading to coagulation during the acrylic polymerisation). Therefore, a major advantage of employing the PEO-containing polyurethanes of the invention is that they provide sufficient colloid stability to allow the incorporation of acid functional comonomers).

Examples of vinyl monomers which may be used to form the vinyl polymer include 1,3-butadiene, isoprene, styrene,  $\alpha$ -methyl styrene, acrylonitrile, methacrylonitrile, vinyl halides such as vinyl chloride, vinyl esters such as vinyl acetate, vinyl propionate, vinyl laurate, and vinyl esters of versatic acid such as VeoVa 9 and VeoVa 10 (VeoVa is a trademark of Shell), heterocyclic vinyl compounds, alkyl esters of mono-olefinically unsaturated dicarboxylic acids (such as di-n-butyl maleate and di-n-butyl fumarate) and, in particular, esters of acrylic acid and methacrylic acid of formula



wherein R<sup>2</sup> is H or methyl and R<sup>3</sup> is optionally substituted alkyl or cycloalkyl of 1 to 20 carbon atoms (more preferably 1 to 8 carbon atoms) examples of which are methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-butyl acrylate, n-butyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, isopropyl acrylate, isopropyl methacrylate, n-propyl acrylate, n-propyl methacrylate, and hydroxyalkyl (meth)acrylates such as hydroxyethyl acrylate, hydroxyethylmethacrylate 2-hydroxypropyl

methacrylate, 2-hydroxypropyl acrylate, and their modified analogues like Tone M-100 (Tone is a trademark of Union Carbide Corporation). Olefinically unsaturated carboxylic acid(s) must of course be employed, e.g. monocarboxylic and/or dicarboxylic acids, such as acrylic acid, methacrylic acid, beta-carboxyethyl acrylate fumaric acid, and itaconic acid. The amount is preferably sufficient to provide an amount of acid monomer(s) within the range of 5 to 40 wt % based on the total weight of vinyl monomers used in the polymerisation.

Particularly preferred are vinyl polymers made from a monomer system comprising at least 40 weight % of one or more monomers of the formula  $\text{CH}_2=\text{CR}^2\text{COOR}^3$  defined above. Such preferred polymers are defined herein as acrylic polymers. More preferably, the monomer system contains at least 50 weight % of such monomers, and particularly at least 60 weight %. The other monomer(s) in such acrylic polymers (if used), besides acid monomers (which are essential as discussed above), may include one or more of the other vinyl monomers mentioned above, and/or may include ones different to such other monomers. Styrene is a useful other monomer. Preferred (meth)acrylic ester monomers include methyl acrylate and ethyl acrylate; others which may be used include methyl methacrylate, n-butyl acrylate, n-butyl methacrylate, and 2-ethylhexyl acrylate.

The glass transition temperature of the vinyl polymer may vary within a wide range, a possible range being from -50 to 120°C. Its number average molecular weight will often be in the range of from 1,000 to 300,000 Daltons. The vinyl polymer is preferably of low number average molecular weight, e.g. in the range 1,000 to 10,000 Daltons, more preferably 1,000 to 5,000 Daltons (and in such cases a chain transfer agent will usually be employed in the vinyl polymerisation).

Neutralisation of the acid groups of the vinyl polymer may be effected at any convenient stage, e.g. before, during, or after admixture with the polyurethane in the case of using a preformed vinyl polymer (and over one or more stages if required). In the case of using in-situ formed vinyl polymer, neutralisation may be effected at any convenient stage of the polyurethane preparation (and over one or more stages if required). In particular, and when feasible, the neutralisation of the vinyl carboxyl groups may be effected concurrently with the acid groups of the polyurethane polymer.

It is to be further understood that the same requirements regarding the nature of the bases (permanent or volatile) apply equally to the neutralisation of carboxyl groups of the vinyl polymer (and in fact, the same base(s) system as used for the polyurethane polymer will often be employed).

It is further to be understood that any reference to a polyurethane film herein includes a film the binder of which optionally contains another polymer besides a polyurethane (as discussed above).

It is to be understood that the film of the invention, except as a possible stage in its production, is not intended to be in the form of a coating on a substrate, i.e. it is "free-standing" and normally self-supporting.

5 Polyurethane films according to the invention could be used to provide packaging film constructions of the monolayer or the laminate type. It would also in principle be possible to employ a laminate film construction of a polyurethane film with a film of a different type, e.g. a PVA film or a carboxylated acrylic film.

10 As discussed above, the invention films are normally made by casting from an aqueous solution, although in principle any other feasible method could be used (such as spraying onto and then removing from a substrate, extrusion of dry polymer, blow film extrusion of dry polymer). When a film is to be made by casting, a solution of the polymer system, together with any desired additive(s), could e.g. be poured onto a suitable mould flat horizontal surface (e.g. made of a plastics, metal, or glass material) and the aqueous carrier phase removed by natural or accelerated evaporation (e.g. at room temperature or  
15 at an elevated temperature as for example in an oven). A film could also be made by casting onto a flat surface (preferably continuous casting on a moving belt) using e.g. an applicator bar to determine film thickness rather than mould dimensions. Laminate films may be formed by techniques such as sequential casting (e.g. by roller coating or using a doctor blade), lamination of two preformed films, and co-extrusion.

20 The water-soluble films of the invention may also include if desired materials such as slip aids, waxes, colourants, wetting agents (surfactants), fillers (e.g. silica or starch); chelating agents, and plasticisers.

The film may also contain a sequestering agent for assisting solubility in tap water (if used to dissolve the film). A sequestering agent could also be present in the packaged  
25 contents (e.g. by adding it to the formulation being packaged) or in the water used to dissolve the film when in use.

Packaging such as a sachet made from the invention polyurethane film can be formed and filled using standard techniques (such as thermoforming or vertical form-fill-sealing).

### 30 General Test for Testing the Solubility of Films in Water

The solubility of the films is determined by mounting the film of whatever thickness in a 35mm slide frame and immersing the slide mount into 500 cm<sup>3</sup> of water (distilled, de-ionised or tap), in a 600 cm<sup>3</sup> beaker, maintained at the temperature at which dissolution is to be tested, usually 10°C. The slide mount is clamped with the film immersed and the  
35 water stirred at 400 rpm using a 2.5 cm length magnetic stirrer bar.

The dissolution time is measured as the time taken for complete dissolution of the film (after breaking free of the slide frame) such that no trace of film remains on the filter sieve when the solution is filtered through a 150 micron mesh sieve.

If the dissolution time is greater than 10 minutes, at the thickness of the film and water temperature employed, the film is deemed to be insoluble for the purposes of the invention.

The present invention is now further illustrated, but in no way limited by reference to the following worked example.

Example 1

To a 1 litre reaction vessel were added 2,2-Bis(hydroxymethyl) propionic acid (DMPA) (50.00g), polypropylene glycol, (MW 1,000; 183.20g) (PPG 1000), polyethylene glycol (MW 1,000; 61.05g) (PEG 1000) and N-methylpyrrolidone (125g), followed by isophorone diisocyanate (IPDI) (205.75g). The contents were stirred under a nitrogen atmosphere and heated to 50°C. At this temperature the catalyst dibutyltin dilaurate (0.50g) was added. The contents were then heated to 90°C and this temperature was maintained for 3 hours. After the formation of urethane prepolymer was complete, the residual isocyanate content was determined (practical wt % = 4.00 against theoretical of 4.14%).

To a separate 2 litre dispersion vessel were added de-ionised water (1,251.67g), sodium hydroxide (42.62g of a 30 wt % solution in water) and hydrazine hydrate (11.03g). The urethane prepolymer (590g) was then added to the dispersion vessel over approximately 4 minutes under low shear conditions to produce a slightly cloudy aqueous urethane solution of solids 25.7 wt % at pH 7.8.

The above recipe can be summarised as follows;

Polymer composition (wt %)

IPDI 41.15

PEG 1000 12.21

PPG 1000 36.64

DMPA 10.00

Catalyst 0.10

NCO : OH ratio = 1.5

Degree of chain-extension : on theoretical NCO = 75.8%

on practical NCO = 78.4%

Film cast from the above aqueous solution was shown to completely dissolve in distilled water (~ 10°C) in less than 60 seconds for a film thickness of 120 µm.

The mechanical properties of the film were determined using an Instron tensometer, with the following results.

	Tensile Strength (Mpa)	Modulus (Mpa)	Elongation to Break (%)
Example 1	22	450	324

CLAIMS

1. Water-soluble film comprising a polyurethane polymer(s) having polyethylene oxide groups and acid-functional groups wherein:
- 5 the polyoxyethylene oxide groups are present in the polyurethane polymer in an amount which is within the range of 5 to 45 wt % based on the weight of polyurethane polymer and have a chain length(s) corresponding to a number average molecular weight within the range of 200 to 5,000 Daltons;
- the acid-functional groups are present in the polyurethane in an amount to provide 15 to
- 10 150 milliequivalents per 100 g of polyurethane polymer;
- at least a proportion of the acid-functional groups are neutralised, such neutralisation being with a base(s) at least a part of which is a non-volatile base(s);
- and said polyurethane polymer is the reaction product of:
- (A) an isocyanate-reactive prepolymer component comprising an isocyanate-
- 15 terminated polyurethane prepolymer, said component being formed from reactants which comprise:
- (i) at least one organic polyisocyanate,
- (ii) at least one isocyanate-reactive compound providing said polyethylene oxide groups in the resulting polyurethane polymer, and
- 20 (iii) at least one isocyanate-reactive compound providing said acid-functional groups in the resulting polyurethane polymer, and
- (B) an active hydrogen component comprising an active hydrogen chain-extending compound(s).
- 25 2. Film according to claim 1 wherein the isocyanate-reactive compound providing acid functional groups is 2,2-dimethylol propionic acid.
3. Film according to either claim 1 or claim 2 wherein the isocyanate-reactive compound providing polyoxyethylene groups is a poly(ethylene glycol).
- 30 4. Film according to any one of claims 1 to 3 wherein the reactants for forming the isocyanate-reactive prepolymer component include an isocyanate-reactive compound(s) which is monofunctional with regard to isocyanate-reactive functionality and acts as a chain-terminating material.
- 35 5. Film according to any one of the preceding claims wherein the chain-extending compound is hydrazine or hydrazine hydrate.



6. Film according to any one of claims 1 to 5 wherein the active hydrogen component includes a reactant which is monofunctional with regard to isocyanate-reactivity and acts as a chain-terminating compound.
- 5 7. Film according to any one of preceding claims wherein said polyurethane polymer also incorporates polypropylene oxide groups.
8. Film according to any one of the previous claims, wherein the polymeric material thereof also includes a carboxyl-functional vinyl (preferably acrylic) polymer, said polymer  
10 preferably being formed in-situ from a monomer system at least part of which is used to provide at least part of a solvent system in the urethane prepolymer formation.
9. Aqueous solution of a polyurethane polymer as defined in any one of one of  
15 claims 1 to 8.
10. Water-soluble packaging, preferably in the form of a sachet, capsule or bag, in which the enveloping film of the sachet comprises a polyurethane polymer film as defined according to any one of claims 1 to 8.
- 20 11. Use of a packaging according to claim 10 for packaging a material.
12. Combination of water-soluble packaging according to claim 10 and a material packaged therein.
- 25 13. Process for the production of an aqueous polyurethane polymer solution, which polyurethane polymer has polyethylene oxide groups and acid-functional groups and wherein:  
the polyethylene oxide groups are present in the polyurethane polymer in an amount which is within the range of 5 to 45 wt % based on the weight of polyurethane polymer  
30 and have a chain length(s) corresponding to a number average molecular weight within the range of 200 to 5,000 Daltons;  
the acid-functional groups are present in the polyurethane in an amount 15 to 150 milliequivalents per 100 g of polyurethane polymer; and  
at least a proportion of the acid-functional groups are neutralised, such neutralisation  
35 being with a base(s) at least a part of which is a non-volatile base(s);  
said process comprising :
- I. synthesising an isocyanate-reactive prepolymer component comprising an isocyanate-terminated polyurethane prepolymer from reactants which comprise :

- 5
- (i) at least one organic polyisocyanate,
  - (ii) at least one isocyanate-reactive compound providing said polyethylene oxide groups in the resulting polyurethane polymer, and
  - (iii) at least one isocyanate-reactive compound providing said acid-functional groups in the resulting polyurethane polymer;
- 10
- II chain extending said prepolymer component using an active hydrogen component comprising an active hydrogen chain extending compound(s) to form said polyurethane polymer; and
  - 10 III forming an aqueous solution of said polyurethane polymer.



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